



DECLARATION

I, Junko Nakamura, of SHIGA INTERNATIONAL PATENT OFFICE, 3-1, Yaesu 2-chome, Chuo-ku, Tokyo, Japan, understand both English and Japanese, am the translator of the English document attached, and do hereby declare and state that the attached English document contains an accurate translation of the official certified copy of Japanese Patent Application No. 11-341443 and that all statements made herein are true to the best of my knowledge.

Declared in Tokyo, Japan

This 24th day of November, 2004

Junko Nakamura

Junko Nakamura



PATENT OFFICE
JAPANESE GOVERNMENT

This is to certify that the annexed is a true copy of the following application as filed with this office.

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Applicant(s): Honda Giken Kogyo Kabushiki Kaisha
Mitsubishi Gas Chemical Co., Inc.

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[Title of the Invention] METHOD FOR STOPPING METHANOL
REFORMING APPARATUS

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[Inventor]

[Address] c/o K.K. Honda Gijutsu Kenkyusho, 4-1, Chuo 1-chome, Wako-shi,
Saitama-ken, Japan

[Name] Takahiro Naka

[Inventor]

[Address] c/o K.K. Honda Gijutsu Kenkyusho, 4-1, Chuo 1-chome, Wako-shi,
Saitama-ken, Japan

[Name] Hideaki Sumi

[Inventor]

[Address] c/o K.K. Honda Gijutsu Kenkyusho, 4-1, Chuo 1-chome, Wako-shi,
Saitama-ken, Japan

[Name] Masataka Furuyama

[Inventor]

[Address] c/o K.K. Honda Gijutsu Kenkyusho, 4-1, Chuo 1-chome, Wako-shi,
Saitama-ken, Japan

[Name] Shoji Isobe

[Inventor]

[Address] c/o Mitsubishi Gas Chemical Co., Inc., Niigata Research Laboratory, 182,
Shinwari, Tayuuhama, Niigata-shi, Niigata-ken, Japan

[Name] Yasushi Hiramatsu

[Inventor]

[Address] c/o Mitsubishi Gas Chemical Co., Inc., Niigata Research Laboratory, 182,
Shinwari, Tayuuhama, Niigata-shi, Niigata-ken, Japan

[Name] Mikio Yoneoka

[Applicant for Patent]

[Identification Number] 000005326

[Name] K.K. Honda Gijutsu Kenkyusho

[Applicant for Patent]

[Identification Number] 000004466

[Name] Mitsubishi Gas Chemical Co., Inc.

[Agent]

[Identification Number] 100064908

[Attorney]

[Name] Masatake Shiga

[Elected Agent]

[Identification Number] 100108578

[Attorney]

[Name] Norio Takahashi

[Elected Agent]

[Identification Number] 100101465

[Attorney]

[Name] Masakazu Aoyama

[Elected Agent]

[Identification Number] 100094400

[Attorney]

[Name] Mitsuyoshi Suzuki

[Elected Agent]

[Identification Number] 100107836

[Attorney]

[Name] Kazuya Nishi

[Elected Agent]

[Identification Number] 100108453

[Attorney]

[Name] Yasuhiko Murayama

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[Item]	Specification	1
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[Item]	Drawing	1
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[Item]	Abstract	1
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Information on Applicant

Identification Number	[000005326]
1. Renewal Date	September 6, 1990
[Reason]	New Registration
Address	1-1, Minamiaoyama 2-chome, Minato-ku, Tokyo, Japan
Name	Honda Giken Kogyo Kabushiki Kaisha

No. 2000-3062372

Information on Applicant

Identification Number	[000004466]
1. Renewal Date	July, 26 1994
[Reason]	Address Alteration
Address	5-2, Marunouchi 2-chome, Chiyoda-ku, Tokyo, Japan
Name	Mitsubishi Gas Chemical Co. Inc.

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[Document type] Specification

[Title of the Invention] METHOD OF STOPPING METHANOL REFORMING
APPARATUS

[Claims]

[Claim 1] A method of stopping a methanol reforming apparatus (23) that generates a hydrogen-rich gas by reacting a mixed gas of water, methanol and air on a catalyst (41), which comprises:

stopping the introduction of air, changing the molar ratio of water/methanol to a value higher than that of steady operation, and stopping the introduction of water and methanol.

[Claim 2] A method of stopping a methanol reforming apparatus according to claim 1, wherein the molar ratio is set to 4.6 or higher.

[Detailed Description of the Invention]

[0001]

[Technical Field of the Invention]

The present invention relates to method of stopping a methanol reforming apparatus that generates a hydrogen enriched gas from water and methanol.

[0002]

[Prior Art]

Fuel cells have been developed as a means for driving low-pollution vehicles and for supplying electric power to vehicles.

Hydrogen in the form of a compressed hydrogen gas or liquid hydrogen is convenient as the energy source for the fuel cell, but there are problems regarding to safety and the ease of handling. Thus there is a demand for a hydrogen supply

apparatus having higher safety.

Recently, technologies for preparing hydrogen enriched gas by reforming alcohol or hydrocarbons using a catalyst have been intensively studied and developed, and various catalysts and reaction apparatuses have been invented.

[0003]

[Problem to be Solved by the Invention]

However, when methanol, which has a low flash point and a low ignition point, is reformed, particularly when employing the autothermal reaction process, wherein a partial oxidization reaction and steam reforming reaction are carried out at the same time, methanol vapor and air coexist on a catalyst that has a high temperature, and therefore the mixing ratio of water, methanol and air must not be within a range in which the reaction proceeds at an excessively high rate (hereinafter this range is referred to as “high-rate reaction region”), and the amounts of these materials to be introduced must be strictly controlled.

[0004]

On the other hand, stopping the operation of the methanol reforming apparatus, the supplies of water, methanol and air are stopped and the catalyst layer is cooled. However, if an excessive amount of air is supplied during the autothermal reaction process, a partial oxidization reaction proceeds, thus giving rise to the possibility of an uncontrolled thermal runaway of the catalyst layer.

[0005]

Therefore, when stopping the methanol reforming apparatus, it is also important to strictly control the mixing ratio of water, methanol and air so as to avoid the high-rate reaction region. Particularly, since the operation must be stopped while controlling the

air supply to a proper level, it takes a long time to stop the operation.

[0006]

The present invention has been made in consideration of the problems described above, and an object thereof is to quickly cool down a catalyst layer without causing thermal runaway when stopping a methanol reforming apparatus.

[0007]

[Means for Solving the Problem]

In order to achieve the objects described above, with the present invention, first the introduction of air is stopped while the introduction of water and methanol to the catalyst layer (reforming catalyst 41 in FIG. 1) is continued, to thereby lower the catalyst layer temperature by making use of the endothermic effect of the methanol steam reforming reaction.

The introduction of air may be stopped either quickly by means of a shut-off valve or gradually by means of a control valve or the like.

[0008]

On the other hand, the catalyst layer temperature can be lowered quickly by setting the molar ratio of water/methanol, which is to be continually introduced after stopping the supply of air, to a molar ratio higher than that of the normal operation (for example, 1.0-2.0) since this accelerates the methanol steam reforming reaction, which is an endothermic reaction.

When the catalyst layer has been cooled down to a predetermined temperature, the introduction of water and methanol is stopped.

If the molar ratio of water/methanol is set to a value outside of the high-rate reaction region in advance before stopping the introduction of fuel, the operation can be

stopped smoothly without causing thermal runaway.

[0009]

The present inventors have found, from the three-component mixture phase diagram of water, methanol and air shown in FIG. 2, that the reaction can be stopped smoothly without allowing the reaction to proceed at a high rate by controlling the mixing ratio of water, methanol and air so as to keep the molar ratio of water/methanol (hereinafter referred to as S/C ratio) at 4.6 (= 82% by mole/18% by mole) or higher. In this drawing, the hatched portion shows the high-rate reaction region.

Therefore, in order to stop the process smoothly, it is preferable to stop the introduction of water and methanol after switching the S/C ratio to 4.5 or higher.

[0010]

[Embodiments of the Invention]

Preferred embodiments of the present invention will now be described below with reference to the accompanying drawings.

(First Embodiment)

FIG. 1 shows a system for supplying fuel to a fuel cell in an electric vehicle, where the reference numeral 10 denotes a fuel cell.

The fuel cell 10 generates electricity by using hydrogen and oxygen that is taken from air as the fuel.

A hydrogen supply system and an air supply system for the fuel cell 10 will be described below.

[0011]

(Hydrogen supply system)

The hydrogen supply system comprises a combustion device 21, an evaporator

22, a reformer (methanol reforming apparatus) 23, a CO eliminator 24, a starting heater 25, heat exchangers 26a, 26b, mixed water-methanol solution tanks 27a, 27b and a methanol tank 28 as major components.

[0012]

The combustion device 21 has an electric heater 31 serving as an ignition device, a combustion catalyst 32 that maintains the state of combustion and a temperature sensor 33 that monitors the temperature inside of the apparatus, wherein methanol supplied from the methanol tank 28 is burned with the air supplied from the air supply system, thereby generating a combustion gas used to warm up the evaporator 22 which evaporates the mixed water-methanol solution that is supplied to the evaporator 22.

[0013]

Connected to the combustion device 21 is an off gas tube 34 provided for the purpose of reusing the off gas that includes hydrogen-rich gas, which is generated in the reformer 23 in the period from the startup to the normal operation, and unreacted hydrogen, which is discharged from the fuel cell 10 during stationary operation, as the fuel for combustion.

[0014]

In the evaporator 22, the mixed water-methanol solution that has been supplied from the mixed water-methanol solution tank 27a where the S/C ratio is controlled to 1.5 or from the mixed water-methanol solution tank 27b where the S/C ratio is controlled to 4.6 is sprayed from a nozzle and evaporated by the combustion gas supplied from the combustion device 21, thereby generating the mixed water-methanol gas.

The evaporator 22 is provided with a temperature sensor 36 for monitoring the temperature inside of the device.

[0015]

Installed in the reformer 23 is a reforming catalyst 41 comprising a honeycomb structure of which surface is coated with a catalyst such as Ni, Ru, Rh, Cu-Zn or the like, so that the mixed water-methanol gas supplied from the evaporator 22 is brought onto the reforming catalyst layer 41 to generate hydrogen-rich gas.

The reforming catalyst layer 41 has an O₂ sensor 42 installed at the inlet thereof, and a temperature sensor 43 installed inside of the reforming catalyst layer 41.

[0016]

In the reformer 23, the autothermal reforming reaction takes place as follows.



The reaction scheme (1) represents the steam reforming reaction by methanol and water that produces the target product of hydrogen.

The reaction scheme (1) represents the reaction of partial oxidization of methanol that produces heat by oxidization reaction which provides for the heat needed in the endothermic reaction represented by reaction scheme (1).

[0017]

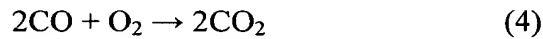
In the reformer 23, in addition to the reactions represented by the reaction schemes (1) and (2), a trace amount of carbon monoxide is generated in an inevitable reaction of methanol decomposition represented as follows.



The carbon monoxide deteriorates Pt catalyst provided in the fuel cell 10 and leads to lower efficiency of power generation and shortens the service life of the cell, and is therefore removed by the CO eliminator 24 installed in a latter stage.

[0018]

The CO eliminator 24 has a selective oxidization catalyst layer made by coating the surface of a honeycomb structure with a catalyst such as Pt or Ru. When hydrogen-rich gas generated by the reformer 23 is supplied, the carbon monoxide is removed from the hydrogen-rich gas in the following reaction of selective oxidization of CO.



[0019]

Installed between the reformer 23 and the CO eliminator 24 is the heat exchanger 26a provided for the purpose of cooling down the hydrogen-rich gas generated by the reformer 23 thereby protecting the selective oxidization catalyst in the CO eliminator 24 from thermal damage. Similarly installed between the CO eliminator 24 and the fuel cell 10 is the heat exchanger 26b provided for the purpose of cooling down the hydrogen-rich gas supplied from the CO eliminator 24 thereby protecting the Pt catalyst in the fuel cell 10 from thermal damage.

[0020]

Valves 51, ..., pumps 55, ... installed in the hydrogen supply system are controlled by an ECU (Electronic Control Unit) 45.

The ECU 45 sends command signals to the valves 51, ..., the pumps 55, ... in accordance to the output signals from the O₂ sensor 42 and the temperature sensor 43 and a stop command, thereby causing these devices to function. The ECU 45 functions also as means for switching the mixed water-methanol solution tanks 27a, 27b that are used as fuel supply sources.

[0021]

(Air supply system)

The air supply system comprises a PCU 61, a drive motor 62, a super charger 63, an inter cooler 64 and filters 65a, 65b as major components, and supplies air, that is introduced from the outside, to the fuel cell 10, the combustion device 21 and the starting heater 25.

Main function of the PCU 61 is to adjust the output of the drive motor 62, by regulating the electric power supplied from the fuel cell 10 and supplies the regulated power to the drive motor 62.

[0022]

The super charger 63 compresses the air taken from the outside through the filter 65a, via a resonator 66.

The inter cooler 64 is provided for cooling down the air that has been heated through compression by the super charger 63. The cooled air passes through the filter 65b, which is installed in the latter stage of the inter cooler 64, and is supplied to the fuel cell 10, the combustion device 21 and the starting heater 25.

[0023]

The method of stopping the reformer 23 according to the present embodiment will now be described below. Before the description, an example of steady operation (normal reforming operation) will be outlined.

During steady operation, the valve 50 is open so that air from the air supply system, namely the air that has been introduced through the resonator 66 and the filter 65a, cooled by the inter cooler 64 and has passed through the filter 65b, is supplied to the combustion device 21 and the evaporator 22, the reformer 23, ..., that are installed in the latter stage thereof.

[0024]

With the valve 51 being closed and the valve 52 open, the pump 56 supplies the mixed water-methanol solution with the S/C ratio controlled to 1.5 from the mixed water-methanol solution tank 27a to the evaporator 22, so that the mixed water-methanol solution is sprayed from the nozzle into the evaporator 22.

In the evaporator 22, the mixed water-methanol solution is evaporated by the combustion gas supplied from the combustion device 21, thereby generating the mixed water-methanol gas which is supplied to the reformer 23.

[0025]

In the reformer 23, the mixed water-methanol gas is passed through the reforming catalyst 41 to produce hydrogen-rich gas through the reactions of the reaction schemes (1) and (2).

The hydrogen-rich gas produced in the reformer 23 is cooled down from about 300°C to about 100°C while passing through the heat exchanger 26a, to be supplied to the CO eliminator 24.

In the CO eliminator 24, carbon monoxide is removed in the reaction of the reaction scheme (4) by passing the hydrogen-rich gas through the selective oxidization catalyst layer.

[0026]

The hydrogen-rich gas with CO removed therefrom is cooled down from about 180°C to about 80°C while passing through the heat exchanger 26b, and is then supplied to the fuel cell 10.

In the fuel cell 10, the hydrogen-rich gas supplied from the hydrogen supply system and air supplied from the air supply system are used to generate electricity.

While the fuel cell 10 discharges the off gas that includes unreacted hydrogen,

the off gas is returned through an off gas tube to the combustion device 21 and is reused as the fuel of combustion.

[0027]

Now the method to stop the steady operation of the reformer 23 will be described below.

This reformer stopping method comprises a first step in which the introduction of air to the reformer 23 is stopped, a second step in which the S/C ratio of mixed water-methanol gas supplied to the reformer 23 is changed to a value higher than that of the steady operation, and a third step in which the introduction of the mixed water-methanol gas to the reformer 23 is stopped.

[0028]

In the first step, the valve 50 that has been open during the steady operation is closed.

This shuts off the introduction of air from the air supply system to the hydrogen supply system, namely to the combustion device 21 and the evaporator 22, the reformer 23, ..., that are installed in the latter stage thereof.

At this time, since the ratio of air in the mixture decreases in comparison to water and methanol in the reformer 23, the endothermic reaction of the reaction scheme (1) proceeds while the exothermic reaction of the reaction scheme (2) is suppressed. As a result, the reforming catalyst layer 41 is effectively cooled.

[0029]

In the second step, the valve 52 that has been open during the steady operation is closed and the valve 51 that has been closed is opened.

This causes the pump 55 to supply the mixed water-methanol solution with the

S/C ratio controlled to 4.6 from the mixed water-methanol solution tank 27b to the evaporator 22, so that the mixed water-methanol gas generated through evaporation in the evaporator 22 is supplied to the reformer 23.

At this time, since the S/C ratio of the mixed water-methanol gas is set higher than that of the steady operation (for example, $S/C = 1.0-2.0$), the endothermic reaction of the reaction scheme (1) is accelerated so that the reforming catalyst layer 41 is cooled down quickly.

[0030]

Last, in the third step, when the reforming catalyst layer 41 is cooled down to a predetermined temperature, the valve 51 that was opened in the second step is closed.

This shuts off the supply of the mixed water-methanol solution from the mixed water-methanol solution tank 27b to the evaporator 22 and stops the introduction of the mixed water-methanol gas to the reformer 23.

At this time, since the S/C ratio is set to a value outside of the high-rate reaction region (refer to FIG. 2), the process can be stopped smoothly without causing thermal runaway.

[0031]

(Second Embodiment)

Second embodiment of the present invention will be described below with reference to FIG. 3. Identical components to those shown in FIG. 1 will be assigned with the same reference numerals and description thereof will be omitted.

This embodiment is the same as the First Embodiment, except for a part of the hydrogen supply system and a part of the air supply system which are different from those of the First Embodiment.

[0032]

The hydrogen supply system has a condenser 71 and an S/C control tank 72 instead of the mixed water-methanol solution tank 27b where the S/C ratio is controlled to 4.6 shown in FIG. 1.

The condenser 71 recovers water, that is generated in the reaction and combustion in the fuel cell 10, from the evaporator 22.

In the S/C control tank 72, mixed water-methanol solution (S/C ratio 4.6 or higher) used in start/stop operation is prepared from the mixed water-methanol solution (S/C ratio 1.5) supplied from the mixed water-methanol solution tank 27a and the recovered water supplied from the condenser 71.

[0033]

S/C ratio of the liquid in the S/C control tank 72 is constantly monitored by a methanol sensor 73 of which signal is sent to the ECU 45.

The ECU 45 controls the extents of opening of valves 75, 76 according to the signal.

After the preparation of the mixed water-methanol solution by the S/C control tank 72 and when the operation is stopped, excessive recovered water in the condenser 71 is discarded.

[0034]

The air supply system has an air supply line 81 connected to the evaporator 22.

Accordingly, the evaporator 22 also serves as a heater that heats the air supplied via the air supply line 81.

Consequently, in this embodiment, the starting heater 25 shown in FIG. 1 is not necessary since the reformer 23 can be warmed up by the heated air.

[0035]

With this constitution, described above, the S/C ratio can be also changed in the second step by switching the mixed water-methanol solution tank 27a for the normal reforming process and the S/C control tank 72 for the start/stop operation when stopping the operation of the reformer 23, and therefore it is made possible to immediately supply the mixed water-methanol gas that has a composition which does not fall in the high-rate reaction region even when stopping the operation of the reformer 23 when the control tends to be unstable. Thus the reforming catalyst layer 41 can be cooled down smoothly and quickly, without causing thermal runaway of the reforming catalyst layer 41.

[0036]

(Example 1)

Using a test apparatus equipped with a reactor tube made of quartz having inner diameter of 20 mm that was filled with 9.2 g of methanol reforming catalyst pellets including Cu, Zn and Al in the ratio of 1.3: 1: 0.05, heated air was introduced to the catalyst at a flow rate of 40 ml/min thereby heating the catalyst to 230°C.

Meanwhile, the mixed water-methanol solution of which S/C ratio was regulated to 1.5 was supplied to the evaporator.

[0037]

The mixed water-methanol gas generated in the evaporator was supplied to the catalyst at a flow rate of 1.8 ml/min thereby starting the reforming reaction by the autothermal reaction method.

Amount of the air introduced was controlled to keep the catalyst layer at 230°C

and the reforming reaction was stabilized.

Then to stop the process, the supplies of water, methanol and air were stopped simultaneously while recording the changes in the catalyst temperature (plots \blacklozenge in FIG. 5).

[0038]

(Example 2)

Using the same test apparatus as in Example 1, the reforming reaction was started and stabilized in the same procedure as in Example 1.

Then to stop the process, first the supplies of water and methanol were stopped and then the supply of air was stopped, while recording the changes in the catalyst temperature (plots \square in FIG. 4).

[0039]

(Example 3)

Using the same test apparatus as in Example 1, the reforming reaction was started and stabilized in the same procedure as in Example 1.

Then to stop the process, first the supply of air was stopped and then the supplies of water and methanol were stopped, while recording the changes in the catalyst temperature (plots \triangle in FIG. 4).

[0040]

(Example 4: present invention)

Using the same test apparatus as in Example 1, the reforming reaction was started and stabilized in the same procedure as in Example 1.

Then to stop the process, first the supply of air was stopped and then the S/C ratio of water and methanol being supplied continuously was changed to 4.6, while

recording the changes in the catalyst temperature (plots ○ in FIG. 4).

[0041]

In contrast to the case where the supplies of water, methanol and air were stopped simultaneously and the catalyst layer was cooled naturally as in Example 1, it was found that stopping the supplies of water and methanol first as in Example 2 resulted in excessive heat generation of the residual methanol and sudden rise in the catalyst layer temperature.

This is because excessive amount of air was supplied to the catalyst layer, thus causing the exothermic reaction of the reaction scheme (2) to proceed at a high rate.

[0042]

When the supply of air was stopped first, as in Example 3, it was found that the catalyst could be cooled down more quickly than in the case of natural cooling due to the endothermic reaction accompanying the reforming of steam by water and methanol.

This is because the endothermic reaction of the reaction scheme (1) proceeds while the exothermic reaction of the reaction scheme (2) is suppressed.

[0043]

When the S/C ratio of water and methanol was changed to a value outside of the high-rate reaction region after stopping the supply of air (or at the same time as the supply of air is stopped) as in Example 4, it was confirmed that the catalyst could be cooled down more quickly than in the case of Example 3.

This is because the endothermic reaction of the reaction scheme (1) is accelerated further while the exothermic reaction of the reaction scheme (2) is suppressed due to the supply of water-rich fuel.

[0044]

As is apparent from the comparison of Examples 1 to 4, it is confirmed that the catalyst can be cooled down smoothly and quickly without causing thermal runaway, when the operation of the reformer 23 is stopped by first stopping the supply of air, then changing the S/C ratio of water and methanol to a value outside of the high-rate reaction region, and last stopping the supplies of water and methanol.

[0045]

[Advantage Effects of the Invention]

The present invention has the following effects.

- (a) Operation of the methanol reforming apparatus is stopped by first stopping the introduction of air and then, after changing the molar ratio of water/methanol to a value higher than that of normal operation, the introduction of water and methanol is stopped. As a result, it is made possible to cause the steam reforming reaction which is an endothermic reaction to proceed while suppressing the partial oxidization reaction which is an exothermic reaction, by first stopping the introduction of air and, moreover, the endothermic reaction can be further accelerated by the change of the molar ratio of water/methanol that is subsequently made.

As a result, the catalyst temperature can be lowered quickly and the time required to stop the operation can be reduced.

[0046]

- (b) Since the introduction of water and methanol is stopped after switching the value of the molar ratio of water/methanol to 4.6 or higher, clear of the high-rate reaction region, when stopping the methanol reforming apparatus, the process can be stopped smoothly without causing thermal runaway.

[Brief Description of the Drawings]

[FIG. 1] FIG. 1 shows a system for supplying fuel to a fuel cell in an electric vehicle according to the present invention.

[FIG. 2] FIG. 2 is a three-component mixture phase diagram of water, methanol and air.

[FIG.3] FIG. 3 shows a system for supplying fuel to a fuel cell in an electric vehicle according to Second Embodiment of the present invention.

[FIG. 4] FIG. 4 shows a change in the temperature of a catalyst measured using a test apparatus.

[Description of Reference Symbols]

23: reformer (methanol reforming apparatus); 41: reforming catalyst

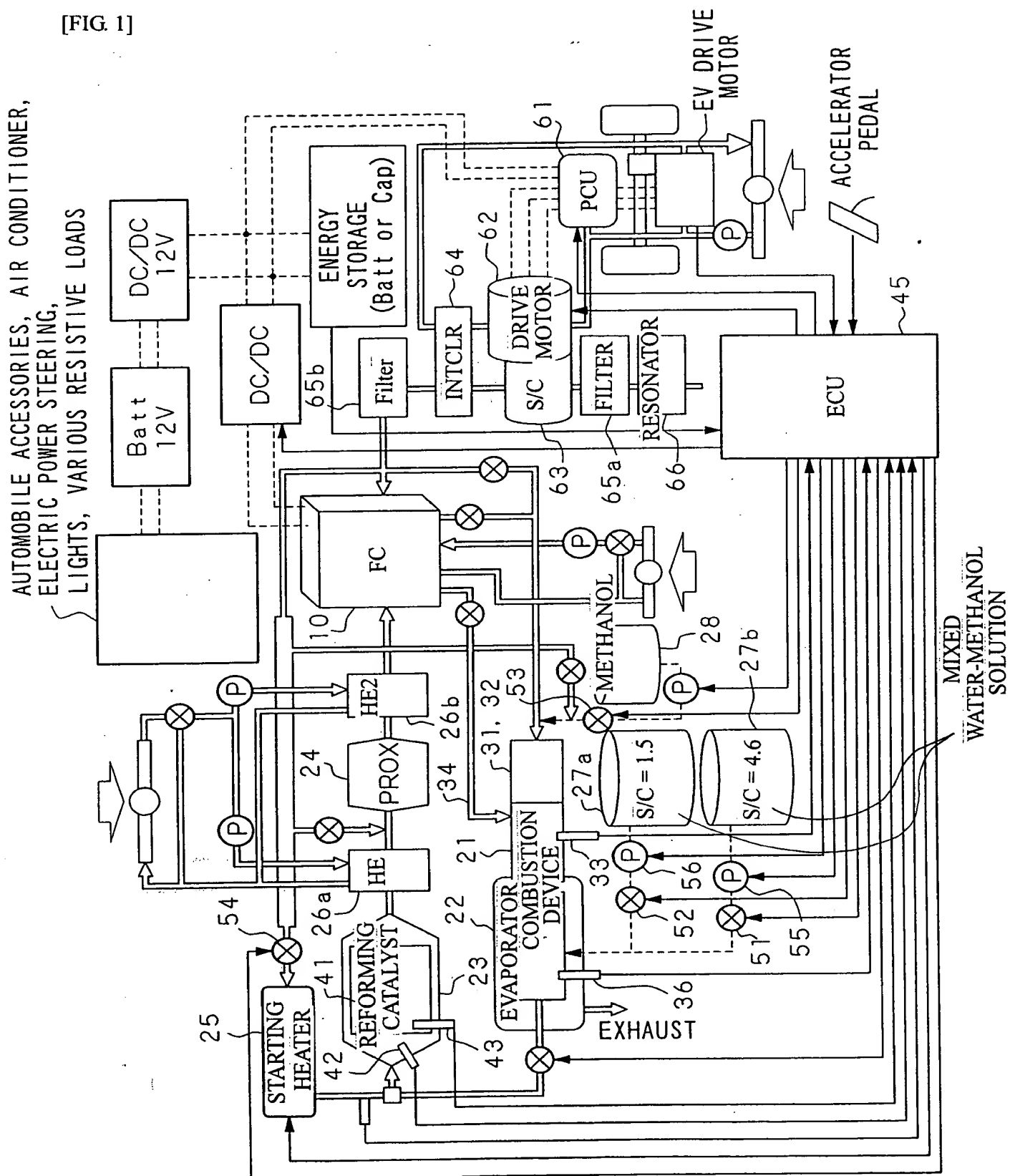
[Document Type] Abstract

[Abstract]

[Problem to be Solved by the Invention] To cool down a catalyst layer without thermal runaway when stopping a methanol reforming apparatus.

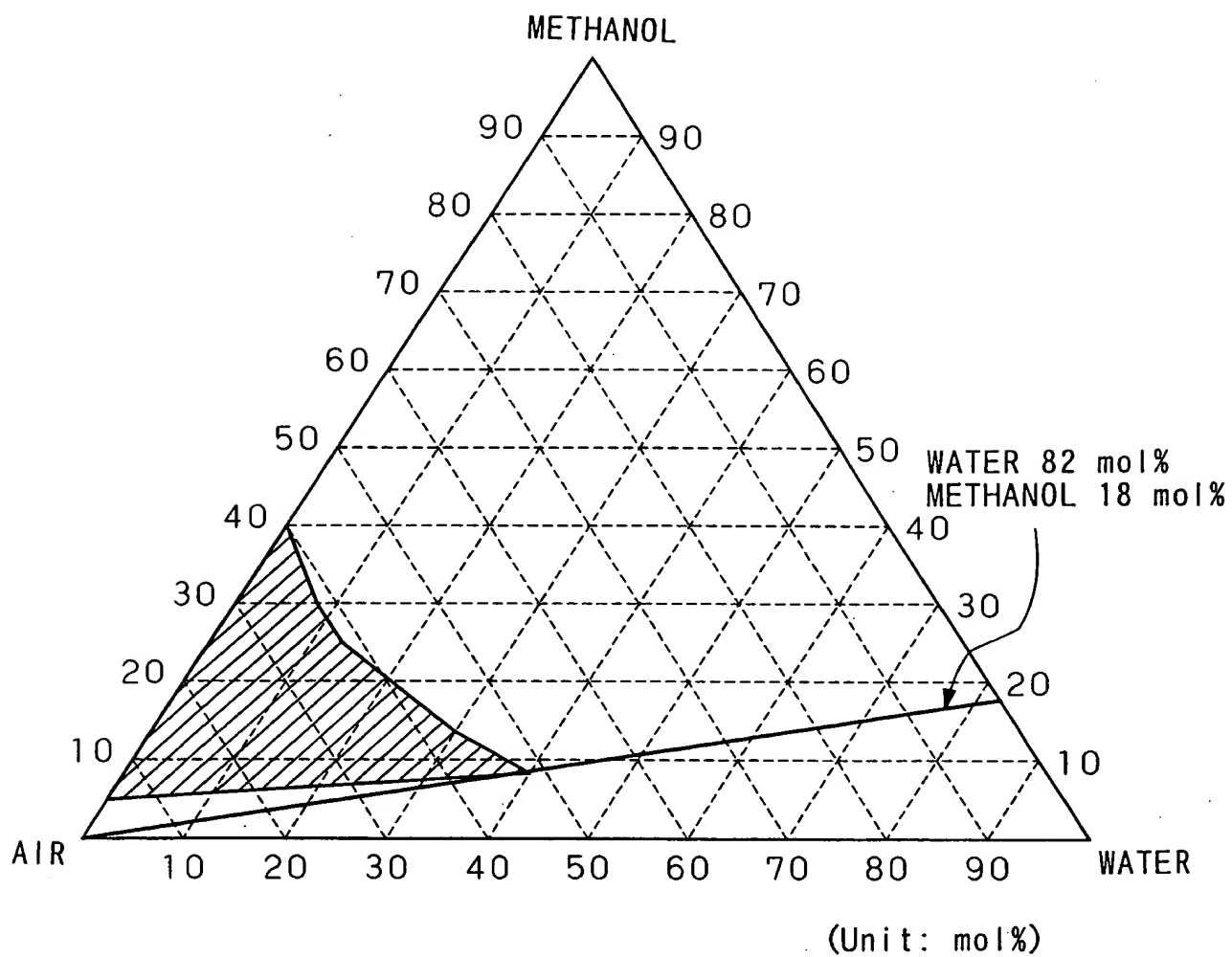
[Means for Solving the Problem] Operation of the methanol reforming apparatus (23) is stopped by first stopping the introduction of air, and a steam reforming reaction which is an endothermic reaction proceeds while suppressing a partial oxidization reaction which is an exothermic reaction. Then the molar ratio of water/methanol is changed to a value higher than that of normal operation (for example, 1.0-2.0), and the exothermic reaction proceeds furthermore. After that, the introduction of water and methanol is stopped. According to the steps, the catalyst layer (41) may cool down quickly. The molar ratio of water/methanol is set to a value (for example, 4.6) outside of the high-rate reaction region, and the operation can be stopped smoothly.

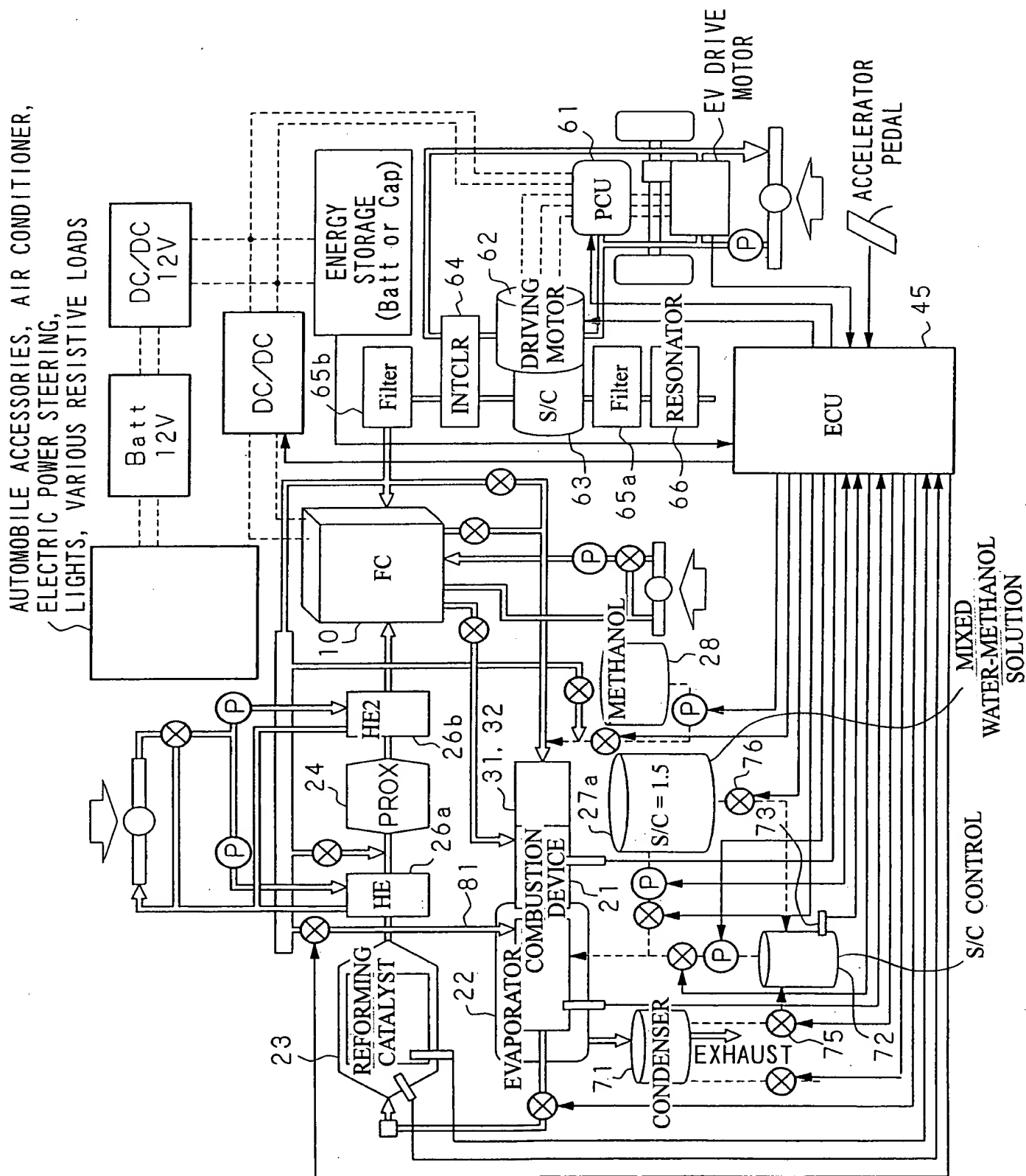
[Selected Drawing] FIG. 1





[FIG. 2]







Docket Number J81061A1

[Document Type] Drawing

[FIG. 4]

